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(71)Applicant : SANTOKU KINZOKU KOGYO KK

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(72)Inventor : MUROTA TADATOSHI  
YAMAMOTO KAZUHIRO  
HASEGAWA TAKASHI  
AOZASA SHIGERU

(54) CERIUM-AND-ZIRCONIUM CONTAINING MULTIPLE OXIDE HAVING HIGH-TEMPERATURE DURABILITY AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To produce a new cerium- and zirconium-contg. multiple oxide having especially superior high-temp. durability by specifying the specific surface area of a multiple oxide contg. zirconium oxide and rare earth metals including cerium.

CONSTITUTION: This multiple oxide contg. >20 to 95% zirconium oxide based on the total weight and rare earth metals including cerium has  $\geq 10\text{m}^2/\text{g}$  specific surface area and exhibits high-temp. durability when heated at  $900^\circ\text{C}$  for 5hr and it is very useful in the field of catalysts and the field of ceramics in place of conventional cerium oxide. This cerium- and zirconium-contg. multiple oxide having superior high-temp. durability is easily produced with high reproducibility.

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(71) 出願人 000176660

三徳金属工業株式会社

兵庫県神戸市東灘区深江北町4丁目14番34号

(72) 発明者 室田 忠俊

神戸市東灘区深江北町4丁目14番34号 三徳金属工業株式会社内

(72) 発明者 山本 和弘

神戸市東灘区深江北町4丁目14番34号 三徳金属工業株式会社内

(74) 代理人 弁理士 酒井 一 (外1名)

最終頁に続く

(54) 【発明の名称】 高温耐久性を有するセリウム及びジルコニウム含有複合酸化物及びその製造法

(57) 【要約】

【構成】 全重量に対して20重量%を越え、95重量%以下の酸化ジルコニウムと、セリウム含有希土類金属とを含む複合酸化物であって、900℃、5時間加熱した際に、比表面積が10m<sup>2</sup>/g以上を示すことを特徴とするセリウム及びジルコニウム含有複合酸化物。

【効果】 本発明のセリウム及びジルコニウム含有複合酸化物は、高温耐久性を有するので、従来の酸化セリウムに代えて触媒分野及びセラミックス分野において極めて有用である。また本発明の製造法では、優れた高温耐久性を有する前記セリウム及びジルコニウム含有複合酸化物を、再現性良く容易に製造することができる。

## 【特許請求の範囲】

【請求項1】 全重量に対して20重量%を越え、95重量%以下の酸化ジルコニウムと、セリウム含有希土類金属とを含む複合酸化物であって、900℃、5時間加熱した際に、比表面積が10m<sup>2</sup>/g以上を示すことを特徴とするセリウム及びジルコニウム含有複合酸化物。

【請求項2】 セリウムイオン及びジルコニウムイオンを含む溶液と、アンモニア水溶液、重炭酸アンモニウム水溶液又は蔞酸水溶液とを混合して、セリウム及びジルコニウム含有複合塩沈殿物を調製した後、該沈殿物に対して少なくとも300℃以上で焼成する工程を行うことを特徴とする請求項1記載のセリウム及びジルコニウム含有複合酸化物の製造法。

## 【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、排ガス清浄用触媒、セラミックス等に利用可能であり、特に優れた高温耐久性を有するセリウム及びジルコニウム含有複合酸化物及びその製造法に関する。

【0002】

【従来の技術】従来、酸化セリウムは、排ガス清浄用触媒、セラミックス等として大量に使用されており、例えば触媒分野においては、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出するという酸化セリウムの特性を利用して、排ガス成分であるHC・CO・NO<sub>x</sub>等に対する浄化率の向上等が行われており、またセラミックス分野においては、前記酸化セリウムの特性を利用して、固体電解質のような導電性セラミックス等に利用されている。このような従来の酸化セリウムは、通常、例えばセリウムの硝酸塩溶液又は塩酸塩溶液に、蔞酸若しくは重炭酸アンモニウムを添加し、得られる沈殿物をろ別、洗浄、乾燥及び焼成する方法等により製造されている。

【0003】しかしながら、前記方法等により製造された従来の酸化セリウムは、比表面積が小さく、特に800℃以上の高温に加熱すると更に小さくなるため、高温耐久性等の性能が大きく劣化するという欠点がある。また優れた高温耐久性を有するセリウム及びジルコニウム含有複合酸化物についても知られていない。

【0004】

【発明が解決しようとする課題】従って本発明の目的は、特に優れた高温耐久性を有する新規なセリウム及びジルコニウム含有複合酸化物及びその製造法を提供することにある。

【0005】本発明の別の目的は、特に優れた高温耐久性を有するセリウム及びジルコニウム含有複合酸化物を、再現性良く、且つ容易に調製することが可能な製造法を提供することにある。

【0006】

【課題を解決するための手段】本発明によれば、全重量

に対して20重量%を越え、95重量%以下の酸化ジルコニウムと、セリウム含有希土類金属とを含む複合酸化物であって、900℃、5時間加熱した際に、比表面積が10m<sup>2</sup>/g以上を示すことを特徴とするセリウム及びジルコニウム含有複合酸化物が提供される。

【0007】また、本発明によれば、セリウムイオン及びジルコニウムイオンを含む溶液と、アンモニア水溶液、重炭酸アンモニウム水溶液又は蔞酸水溶液とを混合して、セリウム及びジルコニウム含有複合塩沈殿物を調製した後、該沈殿物に対して少なくとも300℃以上で焼成する工程を行うことを特徴とする前記セリウム及びジルコニウム含有複合酸化物の製造法が提供される。

【0008】以下本発明を更に詳細に説明する。

【0009】本発明の高温耐久性を有するセリウム及びジルコニウム含有複合酸化物（以下単に複合酸化物1と称す）は、特定量の酸化ジルコニウムとセリウム含有希土類金属とを含んでおり、該酸化ジルコニウムの含有割合は、全重量に対して20重量%を越え、95重量%以下、好ましくは20重量%を越え、80重量%以下含有する。この際、酸化ジルコニウムの含有割合が20重量%以下の場合には十分に性能を発揮することができず、95重量%を越えると比表面積が小さくなる。また前記セリウム含有希土類金属の含有割合は、全重量に対して、好ましくは5～80重量%未満、特に20～80重量%未満が望ましい。本発明の複合酸化物1において、前記セリウム含有希土類金属は、必須成分であるセリウムの他に、ネオジウム、プラセオジウム等の他の希土類金属を含有しても良く、該他の希土類金属の含有割合は、酸化希土類金属として全重量に対して0.1～50重量%であるのが好ましい。

【0010】また本発明の複合酸化物1は、優れた高温耐久性、即ち900℃、5時間加熱後の比表面積が10m<sup>2</sup>/g以上を示せば良く、好ましくは800℃、5時間加熱後において、30m<sup>2</sup>/g以上、特に50m<sup>2</sup>/g以上であるのが望ましい。前記比表面積を測定する方法としては、特に限定されるものではないが、好ましくは公知の方法、例えばmicromeritics社製比表面積自動測定装置、商品名「2200-02型」等で測定することができる。また複合酸化物1の形状は特に限定されるものではないが、例えば球形、立方型等であるのが好ましく、粒径は、0.1～0.5μmであるのが望ましい。

【0011】本発明の複合酸化物1を調製するには、まずセリウムイオン及びジルコニウムイオンを含む溶液とアンモニア水溶液、重炭酸アンモニウム水溶液又は蔞酸水溶液とを混合し、セリウム及びジルコニウム含有複合塩沈殿物を調製する。該セリウムイオン及びジルコニウムイオンを含む溶液は、例えば硝酸セリウム水溶液と硝酸ジルコニウム水溶液とを混合する方法等により得ることができ、またこの際、必要に応じてネオジウムイオン、プラセオジウムイオン等の他の希土類金属イオンを

含む溶液を混合させることもできる。該セリウムイオン及びジルコニウムイオンを含む溶液の濃度は、各イオンを酸化物換算して、好ましくは30~200g/l、特に好ましくは50~100g/lの範囲であり、またセリウムイオン及びジルコニウムイオン、更に必要に応じて添加混合する他の希土類金属イオンの配合割合は、酸化物としての重量比で好ましくは5~80:20~95:0~50、特に好ましくは20~80:80~20:0~20である。更に前記アンモニア水溶液を用いる場合の濃度は、好ましくは1~2N、特に好ましくは1~1.5N、重炭酸アンモニウム水溶液を用いる場合の濃度は、好ましくは50~200g/l、特に好ましくは100~150g/l、蓚酸水溶液を用いる場合の濃度は50~100g/l、特に好ましくは50~60g/lの範囲である。また前記セリウムイオン及びジルコニウムイオンを含む溶液と、アンモニア水溶液、重炭酸アンモニウム水溶液又は蓚酸水溶液との混合割合は、それぞれ重量比で1:1~1:2が好ましい。この際得られる複合塩沈殿物は、例えば複合水酸化物等である。

【0012】次いで前記沈殿物に対して少なくとも、300℃以上、好ましくは300~400℃において焼成する工程を行うことにより本発明の複合酸化物1を製造することができるが、必要に応じて前記沈殿物を予め水熱処理等してから、前記焼成工程を行うこともできる。該水熱処理は、通常のオートクレーブ等により実施でき、その際の温度は100~135℃、処理時間は0.5~1時間の範囲であることが望ましい。前記焼成温度が300℃未満の場合には、酸化物になりにくい。また焼成時間は1~10時間行うのが好ましい。

【0013】本発明の製造法により得られる複合酸化物1は、そのまま使用することもできるが、例えば希土類硝酸塩等を添加して用いることもでき、比表面積は20m<sup>2</sup>/g以上を示すのが好ましい。

【0014】

【発明の効果】本発明のセリウム及びジルコニウム含有複合酸化物は、高温耐久性を有するので、従来の酸化セリウムに代えて触媒分野及びセラミックス分野において極めて有用である。また本発明の製造法では、優れた高温耐久性を有する本発明のセリウム及びジルコニウム含有複合酸化物を、再現性良く容易に製造することができる。

【0015】

【実施例】以下本発明を実施例により更に詳細に説明するが、本発明はこれらに限定されるものではない。

【0016】

【実施例1】高純度硝酸セリウム溶液（三徳金属工業株式会社製、純度99.9%）を水に溶解して調製した、酸化セリウム濃度350g/lの硝酸セリウム水溶液0.107リットルに硝酸ジルコニウム溶液（第一希土元素株式会社製、純度99%）を水に溶解して調製し

た、酸化ジルコニウム（ZrO<sub>2</sub>）濃度25重量%の硝酸ジルコニウム水溶液33ミリリットルとを混合し、ZrO<sub>2</sub>を複合酸化物に対して25重量%とし、複合酸化物濃度50g/lとしたセリウムイオン及びジルコニウムイオン含有溶液を調製した。次いで、得られた溶液1リットルに、別に調製した重炭酸アンモニウム濃度150g/lの重炭酸アンモニウム水溶液1リットルを添加混合し、セリウム及びジルコニウム含有複合炭酸塩沈殿物を80g得た。次いで得られた沈殿物を300℃で5時間焼成し、比表面積90m<sup>2</sup>/gのセリウム及びジルコニウム含有複合酸化物50gを得た。またこの複合酸化物を900℃、5時間加熱した後、比表面積を測定したところ25m<sup>2</sup>/gであった。更に得られた前記複合酸化物中の酸化ジルコニウムの含有割合は25重量%であった。

【0017】

【実施例2】重炭酸アンモニウム水溶液の代わりに、1Nアンモニア水溶液1リットルを添加混合した以外は、実施例1と同様にセリウム及びジルコニウム含有複合酸化物を製造した。得られたセリウム及びジルコニウム含有複合酸化物の900℃、5時間加熱した後の比表面積は27m<sup>2</sup>/gであった。また得られた複合酸化物中の酸化ジルコニウムの含有割合は25重量%であった。

【0018】

【実施例3】重炭酸アンモニウム水溶液の代わりに、40g/l蓚酸水溶液1リットルを添加混合した以外は、実施例1と同様にセリウム及びジルコニウム含有複合酸化物を製造した。得られたセリウム及びジルコニウム含有複合酸化物の900℃、5時間加熱した後の比表面積は、23m<sup>2</sup>/gであった。また得られた複合酸化物中の酸化ジルコニウムの含有割合は25重量%であった。

【0019】

【実施例4】高純度硝酸セリウム溶液を水に溶解して調製した酸化セリウム濃度350g/lの硝酸セリウム水溶液100ミリリットルに、硝酸ジルコニウム溶液を水に溶解して調製した酸化ジルコニウム（ZrO<sub>2</sub>）濃度25重量%の硝酸ジルコニウム水溶液33ミリリットルと、硝酸ネオジウムを水に溶解して調製した酸化ネオジウム濃度200g/lの硝酸ネオジウム水溶液12.5ミリリットルとを混合し、ZrO<sub>2</sub>を複合酸化物に対し25重量%、Nd<sub>2</sub>O<sub>3</sub>を複合酸化物に対し5重量%とし、複合酸化物濃度50g/lとしたセリウムイオン、ジルコニウムイオン及びネオジウムイオン含有溶液を調製した。次いで、得られた溶液1リットルに、別に調製した重炭酸アンモニウム濃度150g/lの重炭酸アンモニウム水溶液1リットルを添加混合し、セリウム、ジルコニウム及びネオジウム含有複合炭酸塩沈殿物を160g得た。次いで得られた沈殿物を300℃で5時間焼成したところ、比表面積90m<sup>2</sup>/gのセリウム、ジルコニウム及びネオジウム含有複合酸化物を50g得た。

またこの複合酸化物を900℃、5時間加熱した後、比表面積を測定したところ31m<sup>2</sup>/gであった。更に得られた前記複合酸化物中の酸化ジルコニウムの含有割合\*

\*は25重量%、酸化ネオジウムの含有割合は5重量%であった。

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(72)発明者 長谷川 剛史

神戸市東灘区深江北町4丁目14番34号 三  
徳金属工業株式会社内

(72)発明者 青笹 繁

神戸市東灘区深江北町4丁目14番34号 三  
徳金属工業株式会社内

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(54) CERIUM-AND-ZIRCONIUM CONTAINING MULTIPLE OXIDE HAVING HIGH-TEMPERATURE DURABILITY AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To produce a new cerium- and zirconium-contg. multiple oxide having especially superior high-temp. durability by specifying the specific surface area of a multiple oxide contg. zirconium oxide and rare earth metals including cerium.

CONSTITUTION: This multiple oxide contg. >20 to 95% zirconium oxide based on the total weight and rare earth metals including cerium has  $\geq 10\text{m}^2/\text{g}$  specific surface area and exhibits high-temp. durability when heated at  $900^\circ\text{C}$  for 5hr and it is very useful in the field of catalysts and the field of ceramics in place of conventional cerium oxide. This cerium- and zirconium-contg. multiple oxide having superior high-temp. durability is easily produced with high reproducibility.

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CLAIMS

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[Claim(s)]

[Claim 1] A cerium and a zirconium content multiple oxide which are a multiple oxide which exceeds 20 % of the weight to total weight, and contains 95 or less % of the weight of zirconium oxide and a cerium content rare earth metal, and are characterized by 900 degrees C of things for which specific surface area shows more than 10m<sup>2</sup>/g when it heats for 5 hours.

[Claim 2] A manufacturing method of a cerium according to claim 1 characterized by performing a production process calcinated above at least 300 degrees C to this precipitate after mixing a solution containing cerium ion and zirconium ion, and an aqueous ammonia solution, an ammonium bicarbonate aqueous solution or an oxalic acid aqueous solution and preparing a cerium and zirconium content compound salt precipitate, and a zirconium content multiple oxide.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the cerium which has the elevated-temperature endurance which is available to the catalyst for exhaust gas clarification, the ceramics, etc., and was especially excellent in them, a zirconium content multiple oxide, and its manufacturing method.

[0002]

[Description of the Prior Art] Conventionally, cerium oxide is used in large quantities as the catalyst for exhaust gas clarification, ceramics, etc. For example, in the catalyst field, oxygen is absorbed under an oxidizing atmosphere, and improvement of the rate of purification to HC-CO-NO<sub>x</sub> which is an exhaust gas component etc. is performed using the property of the cerium oxide of emitting oxygen under reducing atmosphere, and it is used for conductive ceramics like a solid electrolyte etc. in the ceramic field using the property of said cerium oxide. Such conventional cerium oxide is manufactured by the method of adding oxalic acid or ammonium bicarbonate in the nitrate solution or hydrochloride solution of a cerium, and usually washing, drying and calcinating the settlings obtained a \*\* exception etc.

[0003] However, since it will become still smaller if the conventional cerium oxide manufactured by said method etc. has a small specific surface area and is heated especially to an elevated temperature 800 degrees C or more, it has the defect that engine performance, such as elevated-temperature endurance, deteriorates greatly. Moreover, it is not known about the cerium and zirconium content multiple oxide which have the outstanding elevated-temperature endurance, either.

[0004]

[Problem(s) to be Solved by the Invention] Therefore, especially the purpose of this invention is to offer the new cerium which has the outstanding elevated-temperature endurance, a zirconium content multiple oxide, and its manufacturing method.

[0005] Especially another purpose of this invention is to offer the manufacturing method which can prepare often [ repeatability ] and easily the cerium and zirconium content multiple oxide which have the outstanding elevated-temperature endurance.

[0006]

[Means for Solving the Problem] According to this invention, 20 % of the weight is exceeded to total weight, it is a multiple oxide containing 95 or less % of the weight of zirconium oxide and a cerium content rare earth metal, and 900 degrees C of ceriums and zirconium content multiple oxides which are characterized by specific surface area showing more than 10m<sup>2</sup>/g are offered when it heats for 5 hours.

[0007] Moreover, according to this invention, after mixing a solution containing cerium ion and zirconium ion, and an aqueous ammonia solution, an ammonium bicarbonate aqueous solution or an oxalic acid aqueous solution and preparing a cerium and zirconium content compound salt precipitate, a manufacturing method of said cerium characterized by performing a production process calcinated above at least 300 degrees C to this precipitate and a zirconium content multiple oxide is offered.

[0008] This invention is further explained to details below.

[0009] Zirconium oxide and a cerium content rare earth metal of the amount of specification are included, a cerium and a zirconium content multiple oxide (a multiple oxide 1 is only called below) which have the elevated-temperature endurance of this invention exceed 20 % of the weight to total weight, and 95 or less % of the weight, a content rate of this zirconium oxide exceeds 20 % of the weight preferably, and they contain it 80 or less % of the weight. Under the present circumstances, if engine performance cannot fully be demonstrated but 95 % of the weight is exceeded when a content rate of zirconium oxide is 20 or less % of the weight, specific surface area will become small. Moreover, a



content rate of said cerium content rare earth metal has less than 20 - 80 especially preferably desirable % of the weight less than 5 to 80% of the weight to total weight. In the multiple oxide 1 of this invention, said cerium content rare earth metal may contain other rare earth metals other than a cerium which is an indispensable component, such as neodymium and PURASEOJIUMU, and, as for a content rate of these other rare earth metals, it is desirable that it is 0.1 - 50 % of the weight to total weight as an oxidation rare earth metal.

[0010] Moreover, as for the multiple oxide 1 of this invention, it is desirable after 800 degrees C and 5-hour heating for specific surface area after outstanding elevated-temperature endurance, i.e., 900 degrees C, and 5-hour heating to be more than 50m<sup>2</sup>/g especially preferably that what is necessary is just to show more than 10m<sup>2</sup>/g more than 30m<sup>2</sup>/g. Especially as a method of measuring said specific surface area, although not limited, it can measure by desirable well-known method, for example, specific-surface-area automatical measurement equipment made from micromeritics, a trade name "2200-02 Mold", etc. Moreover, although especially a configuration of a multiple oxide 1 is not limited, it is desirable that they are a globular form, a cube mold, etc., for example, and, as for particle size, it is desirable that it is 0.1-0.5 micrometers.

[0011] In order to prepare the multiple oxide 1 of this invention, a solution which contains cerium ion and zirconium ion first, an aqueous ammonia solution, an ammonium bicarbonate aqueous solution, or an oxalic acid aqueous solution is mixed, and a cerium and zirconium content compound salt precipitate are prepared. A solution which can obtain a solution containing this cerium ion and zirconium ion by a method of mixing for example, a cerium-nitrate aqueous solution and a zirconium-nitrate aqueous solution etc., and contains other rare earth metal ion, such as neodymium ion and PURASEOJIUMU ion, if needed in this case can also be mixed. concentration of a solution containing this cerium ion and zirconium ion -- each ion -- oxide conversion -- carrying out -- desirable -- 30 - 200 g/l -- especially -- desirable -- the range of 50 - 100 g/l -- it is -- moreover, the blending ratio of coal of cerium ion and zirconium ion, and other rare earth metal ion that carries out addition mixing if needed further -- a weight ratio as an oxide -- desirable -- 5-80:20-95:0-50 -- it is 20-80:80-20:0-20 especially preferably. Furthermore, concentration in a case of using said aqueous ammonia solution is desirable, concentration in a case of using especially 1-2 Ns of 1-1.5Ns, and ammonium bicarbonate aqueous solutions preferably is desirable, and concentration in a case of using 100 - 150 g/l and an oxalic acid aqueous solution preferably especially 50 to 200 g/l is the range of 50 - 60 g/l especially preferably 50 to 100 g/l. Moreover, as for a mixed rate of a solution containing said cerium ion and zirconium ion, and an aqueous ammonia solution, an ammonium bicarbonate aqueous solution or an oxalic acid aqueous solution, 1:1-1:2 are desirable respectively at a weight ratio. Under the present circumstances, compound salt precipitate obtained is for example, a compound hydroxide etc.

[0012] Subsequently, although the multiple oxide 1 of this invention can be manufactured to said precipitate by performing a production process preferably calcinated in 300-400 degrees C 300 degrees C or more at least, after hydrothermal processing etc. carries out said precipitate beforehand if needed, said baking production process can also be performed. This hydrothermal processing can be carried out with the usual autoclave etc., and it is desirable for temperature in that case to be 100-135 degrees C, and for a range of the processing time to be 0.5 - 1 hour. When said burning temperature is less than 300 degrees C, it is hard to become an oxide. Moreover, as for firing time, it is desirable to carry out for 1 to 10 hours.

[0013] Although the multiple oxide 1 obtained according to a manufacturing method of this invention can also be used as it is, a rare earth nitrate etc. can also be added and used for it, for example, and it is [ specific surface area ] desirable that more than 20m<sup>2</sup>/g is shown.

[0014]

[Effect of the Invention] Since the cerium and zirconium content multiple oxide of this invention have elevated-temperature endurance, they are replaced with conventional cerium oxide and are very useful in the catalyst field and the ceramic field. Moreover, in the manufacturing method of this invention, the cerium and zirconium content multiple oxide of this invention which have the outstanding elevated-temperature endurance can be easily manufactured with sufficient repeatability.

[0015]

[Example] Although an example explains this invention to details further below, this invention is not limited to these.

[0016]

[Example 1] A high grade cerium-nitrate solution (triple-purpose metal industrial stock type company make, 99.9% of purity) is dissolved in water. The cerium ion and zirconium ion content solution which were prepared, which dissolved and prepared the zirconium-nitrate solution (the first rare earth element incorporated company make, 99% of purity) in water at 0.107l. of cerium-nitrate aqueous solutions of cerium oxide concentration 350 g/l and which mixed 33ml of zirconium-nitrate aqueous solutions of 25 % of the weight of zirconium oxide (ZrO<sub>2</sub>) concentration, made ZrO<sub>2</sub> 25 %

of the weight to the multiple oxide, and were made into multiple oxide concentration 50 g/l were prepared. Subsequently, in 1l. of obtained solutions, addition mixing of the 1l. of the ammonium bicarbonate aqueous solutions of ammonium bicarbonate concentration 150 g/l prepared independently was carried out, and a cerium and 80g of zirconium content compound carbonate precipitate were obtained. Subsequently, the obtained sediment was calcinated at 300 degrees C for 5 hours, and the cerium and 50g of zirconium content multiple oxides of specific-surface-area of 90m<sup>2</sup>/g were obtained. Moreover, after heating 900 degrees C of this multiple oxide for 5 hours, when specific surface area was measured, it was 25m<sup>2</sup>/g. Furthermore, the content rate of the zirconium oxide in said obtained multiple oxide was 25 % of the weight.

[0017]

[Example 2] Instead of the ammonium bicarbonate aqueous solution, the cerium and the zirconium content multiple oxide were manufactured like the example 1 except having carried out addition mixing of the 1l. of the 1-N aqueous ammonia solutions. The specific surface area after the obtained cerium and a zirconium content multiple oxide heat 900 degrees C for 5 hours was 27m<sup>2</sup>/g. Moreover, the content rate of the zirconium oxide in the obtained multiple oxide was 25 % of the weight.

[0018]

[Example 3] Instead of the ammonium bicarbonate aqueous solution, the cerium and the zirconium content multiple oxide were manufactured like the example 1 except having carried out addition mixing of the 1l. of the 40 g/l oxalic acid aqueous solutions. The specific surface area after the obtained cerium and a zirconium content multiple oxide heat 900 degrees C for 5 hours was 23m<sup>2</sup>/g. Moreover, the content rate of the zirconium oxide in the obtained multiple oxide was 25 % of the weight.

[0019]

[Example 4] A zirconium-nitrate solution is dissolved in 100ml of cerium-nitrate aqueous solutions with a cerium oxide concentration of 350g [l. ] which dissolved in water and prepared the high grade cerium-nitrate solution at water. 33ml of prepared zirconium-nitrate aqueous solutions of 25 % of the weight of zirconium oxide (ZrO<sub>2</sub>) concentration and 12.5ml of nitric-acid neodymium aqueous solutions of oxidation neodymium concentration 200 g/l which dissolved in water and prepared nitric-acid neodymium were mixed, and the cerium ion, zirconium ion, and neodymium ion content solution which made Nd<sub>2</sub>O<sub>3</sub> 5 % of the weight to the multiple oxide 25% of the weight, and made ZrO<sub>2</sub> multiple oxide concentration 50 g/l to the multiple oxide were prepared. Subsequently, in 1l. of obtained solutions, addition mixing of the 1l. of the ammonium bicarbonate aqueous solutions of ammonium bicarbonate concentration 150 g/l prepared independently was carried out, and a cerium, a zirconium, and 160g of neodymium content compound carbonate precipitate were obtained. Subsequently, when the obtained sediment was calcinated at 300 degrees C for 5 hours, 50g of the ceriums, zirconiums, and neodymium content multiple oxides of specific-surface-area of 90m<sup>2</sup>/g were obtained. Moreover, after heating 900 degrees C of this multiple oxide for 5 hours, when specific surface area was measured, it was 31m<sup>2</sup>/g. Furthermore, the content rate of oxidation neodymium of the content rate of the zirconium oxide in said obtained multiple oxide was 5 % of the weight 25% of the weight.

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[Translation done.]